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Designing Composite Resins in the 21st Century: Ending the "End Group" Fallacy

30 Sept 2015

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Outline

- Inspiration from Rising Sciences
- The “End Group” Fallacy
- New Approaches to Composite Resin Design
- Examples: Payoffs and Cautions

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Applied Materials Group

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- Dr. Josiah Reams
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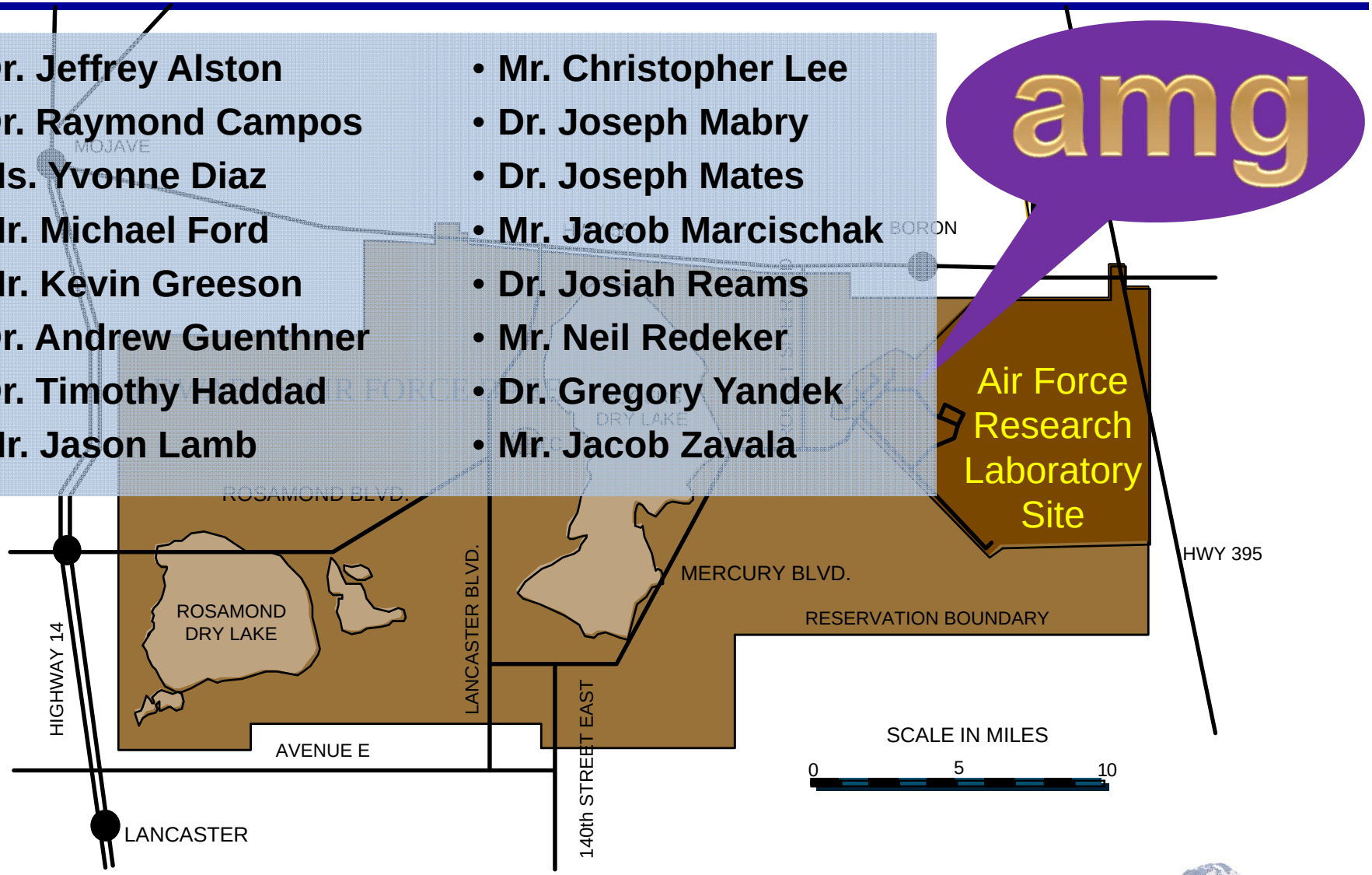
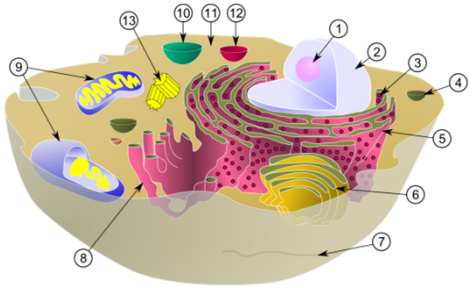


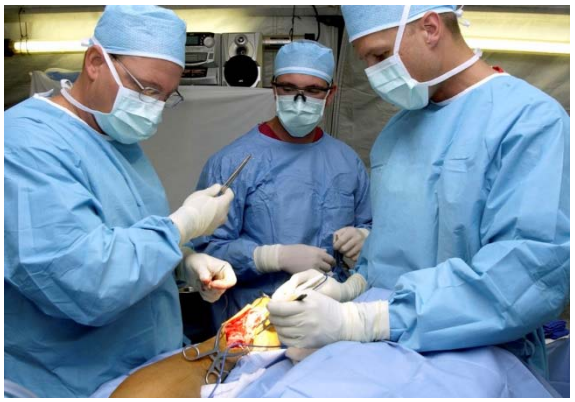
"Rising" Sciences in the 21st Century

- **Biology**



Author: MesserWoland and Szczepan1990

- **Medicine**



US Air Force

Information

- **Digital Matter**

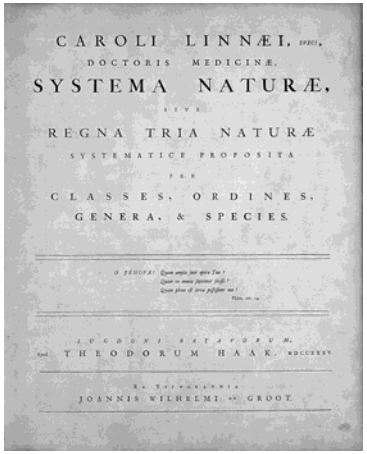
Makerbot Industries

- **Autonomy**

Author: Steve Jurvetson

An Example from Biology

- **100 Years Ago**
  - **System: Linguistic Taxonomy / Inferred Heuristics**
  - **Tools: Microscope, Cell Culture, Notebooks**


CAROLI LINNÆI, MED.
DOCTORIS MEDICINÆ.
SYSTEMA NATURÆ,
REGNA TRIA NATURÆ
SYSTEMATICE PROPOSITA
CLASSES, ORDINES,
GENERA, & SPECIES.
THEODORUM HAAK. MDCCXXXV.
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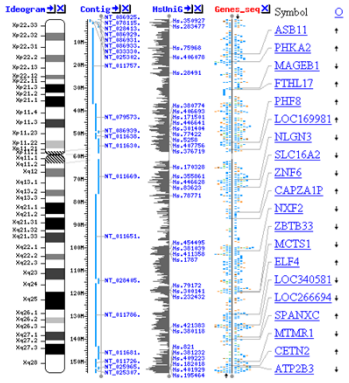
- **Today**
  - **System: Hierarchical Informatics**
  - **Tools: Sequencers, Simulators, Editors, "Big Data" Analytics**



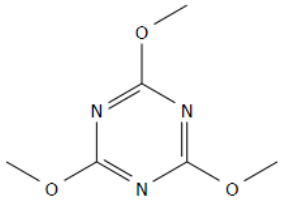
Which one does composite resin chemistry resemble?

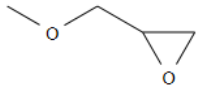
The “End Group Fallacy”

- The “End Group Fallacy” is the bias that results from the current dominant classification and inferred heuristics system for composite resins.
- Resins are described according to a reactive group class, “epoxy”, “BMI”, “polyimide”, with the inference that key properties are shared among members of each group. From the standpoint of how to classify resin systems, such a system is sensible.
- In reality, a very large number of properties, including Tg and TOS, do not fall into separate classes determined by end group chemistry. Rather, many of these properties are sensitive to the topology and architecture of the networks.

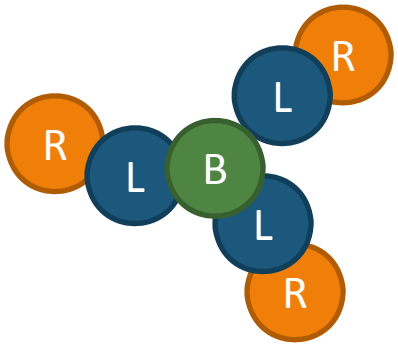
Structure – Architecture - Topology

Structures

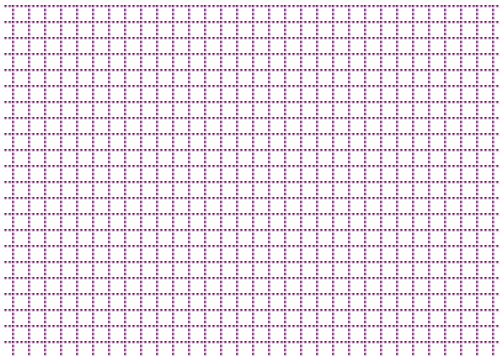


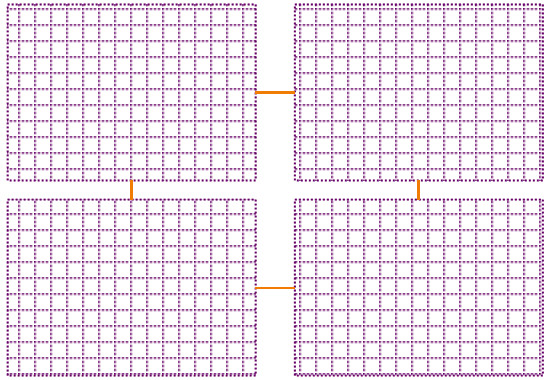


Architectures



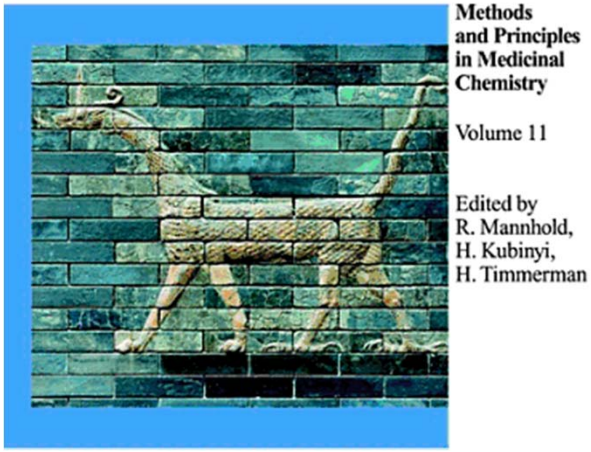
Topologies





- **There are three levels of hierarchy in networks:**
  - ***Structure*** **is the number, type, and geometric relationship of atoms in repeated groups**
  - ***Architecture*** **describes the number, type, and geometric interconnection of repeated structures**
  - ***Topology*** **describes the number, type, and geometric relationship of repeated architectural units**

Digitizing Chemical Structures

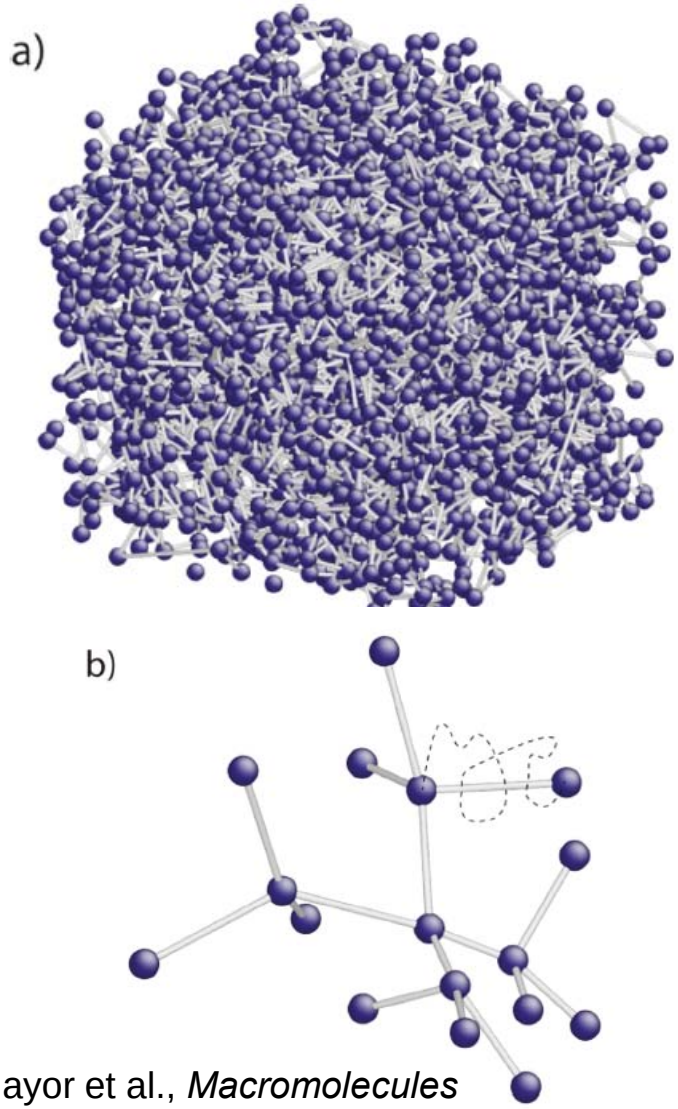


- Methods for converting small molecule chemical structures to strings of information are well-established and in wide use
- Extensions for polymers have been published but are not as extensive
- Further extensions for networks are straightforward, but not much used

How Complex Are Networks?

- Even the most complex cure reactions might have ~100 repeated chemical structures.
- Architectural features can be described in terms of just seven groups
- Topology can be described in terms of a very few parameters (typically 2 or 3)
- A “cheminome” for a composite resin is likely not more than 10,000 units x 10,000 unit scale per each << 10^6 bits
- In reality, most properties are controlled by << 10 units. Modern informatic methods can determine how to construct the units with the most valuable information content.
- Therefore, no reason that chemometrics / informatics cannot be used with composite resins

Network Automata



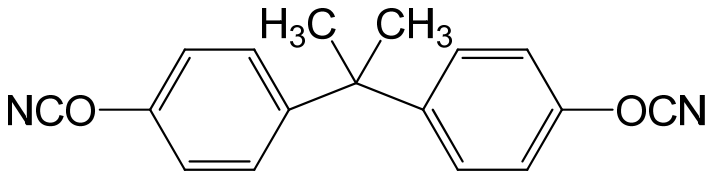
Mayor et al., *Macromolecules* **2011**, *44*, 8106 (LLNL).

- **In correspondence with cellular automata, a system of differential equations describes the evolution of structures, architectures, and topologies in polymer networks**
- **Identical to reaction kinetics at the structural level**
- **Can include mechanical effects**
- **Demonstrated for lightly cross-linked, low Tg networks using several hundred thousand units with sparse topology**

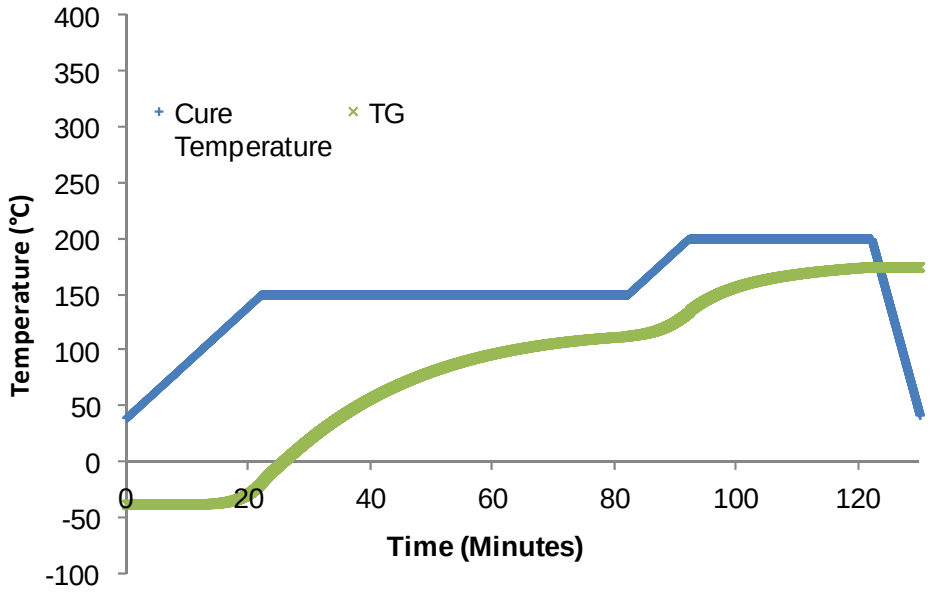
Figure 3. (a) Representation of typical bead–spring cell employed in the mesoscopic model approach. Cross-link junctions are represented schematically as beads connected through springs (straight bars) which serve as the polymer chains. For simplicity of the image, the bead radius has been chosen arbitrarily. (b) Breakout consisting of one central bead connected to nearest and next-nearest neighbors. The dashed line represents schematically the real chain that has been replaced by a single, effective entropic spring with $k = (3k_BT)/(\langle R^2 \rangle)$.

"State of the Art" Network Automata Example

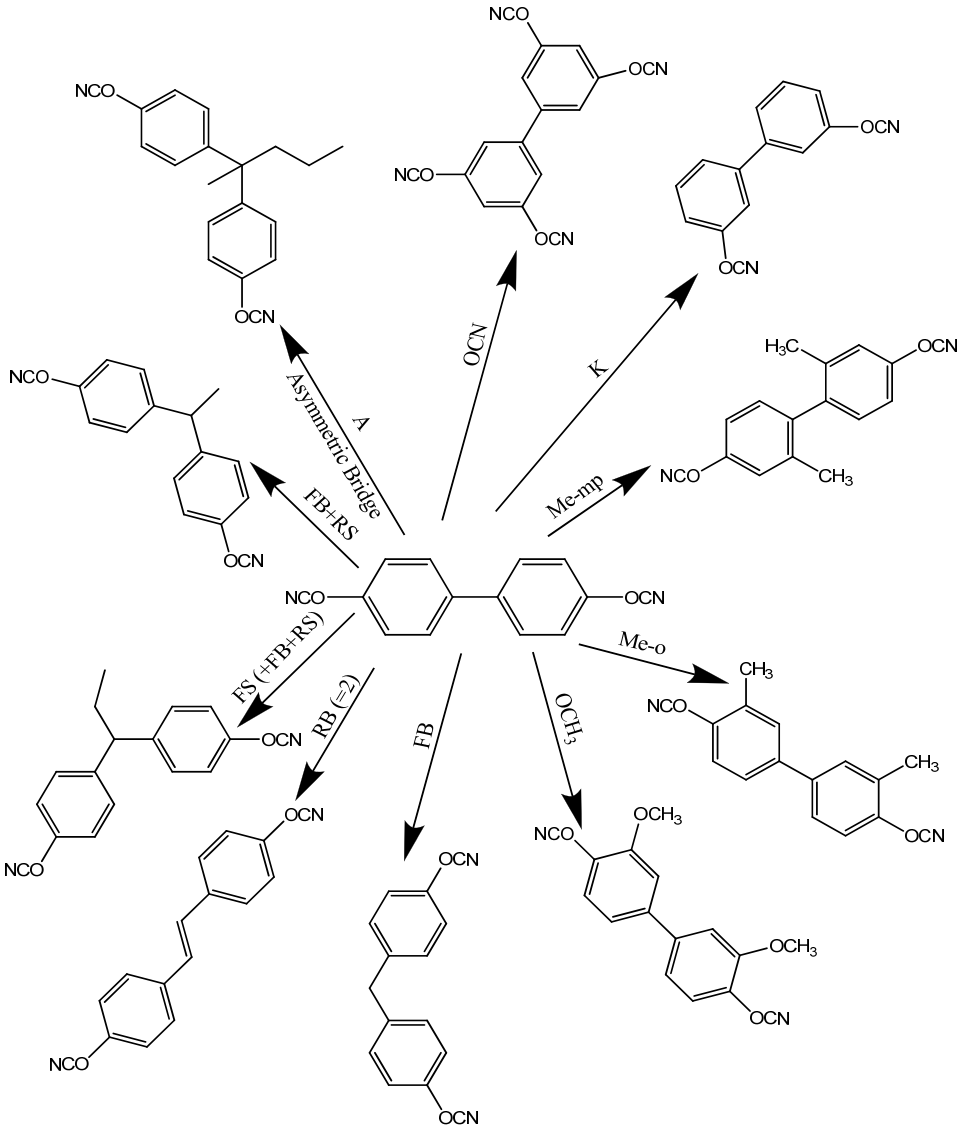
- **Cure kinetics + diBenedetto equation = Tg development kinetics -- 8 parameters predict Tg of network through any process – 6 DSC experiments provide all needed parameters**



Catalyst: 30 : 1 nonylphenol : $Cu(acac)_2$ @ 2 phr (160 ppm Cu)



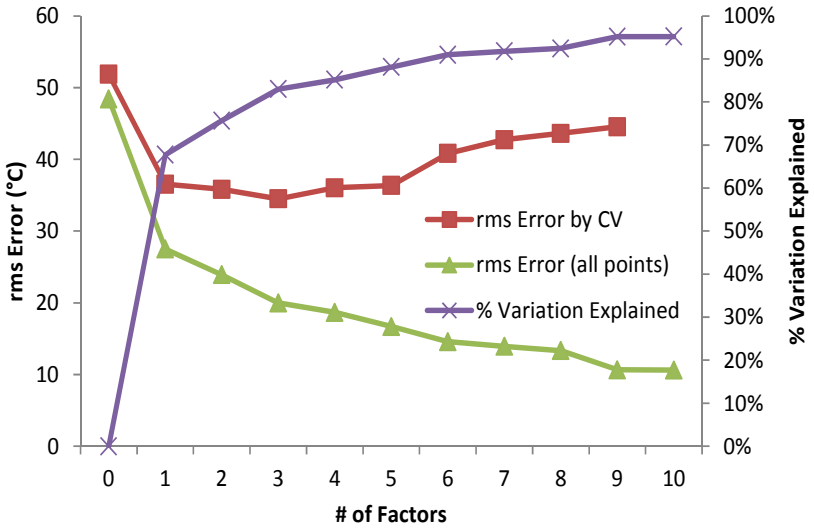
Example: Bio-Based Monomers

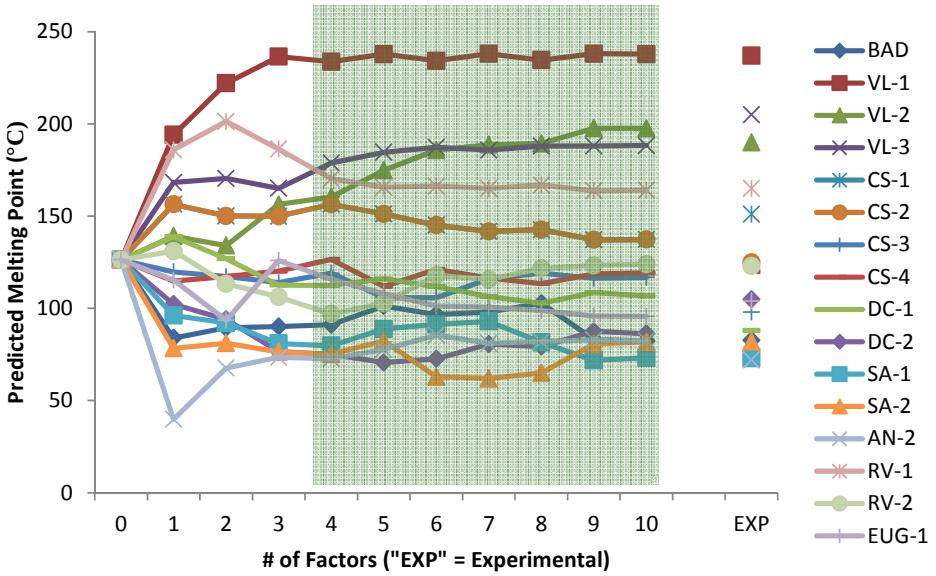


Monomer	OCN	K	Me-mp	Me-o	OCH3	FB	RB	FS	RS	A
BAD	0	0	0	0	0	1	0	0	2	0
LE	0	0	0	0	0	1	0	0	1	1
AN-1	0	0	0	0	0	3	0	1	2	1
AN-2	0	0	0	0	0	0.5	0.5	1.5	3.5	1
CS-1	0	1	1	0	1	1	0	0	0	0
CS-2	0	1	1	0	1	1	0	0	0	0
CS-3	0	1	1	0	1	1	0	0	1	1
CS-4	0	1	1	0	1	1	0	1	1	1
DC-1	0	0	1	0	0	1	0	0	0	0
DC-2	0	0	1	0	0	1	0	0	1	1
DC-3	0	0	1	0	0	1	0	1	1	1
EUG-1	0	0	0	0	1	4	0	0	0	0
RV-1	1	0.5	0	0	0	0	2	0	0	0
RV-2	1	0.5	0	0	0	2	0	0	0	0
SA-1	0	0	0	1	0	1	0	0	1	1
SA-2	0	0	0	1	0	1	0	0	2	0
VL-1	0	0	0	0	1	0	2	0	0	0
VL-2	0	0	0	0	1	2	0	0	0	0
VL-3	0	1	1	0	1	0	0	0	0	0
AN-U	0	0	0	0	0	1	2	1	2	1
EUG-U	0	0	0	0	1	2	0	0	0	0

The structure of bio-based monomers and networks with an X-L-X architecture (X = phenyl cyanate ester / phenyl cyanurate) is quantified using 10 parameters

Predictive Models: Partial Least Squares Approach

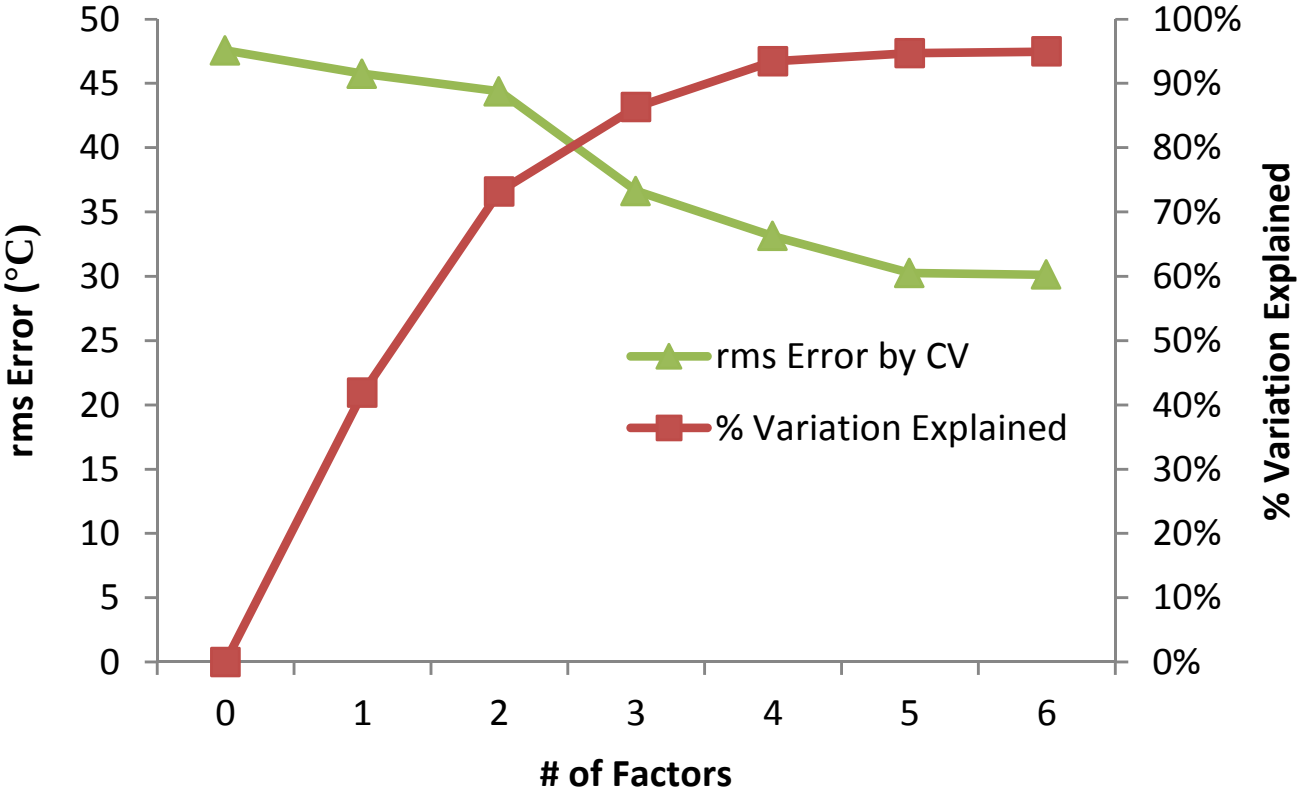




Partial least squares is a typical informatics technique; it looks for correlated parameters that simultaneously describe the most variation in both input and output data sets

The method is iterative; to generate subsequent regression components, the method is repeated for the residuals from the previous set of predicted and experimental values

Predictive Power for Tg at Full Cure

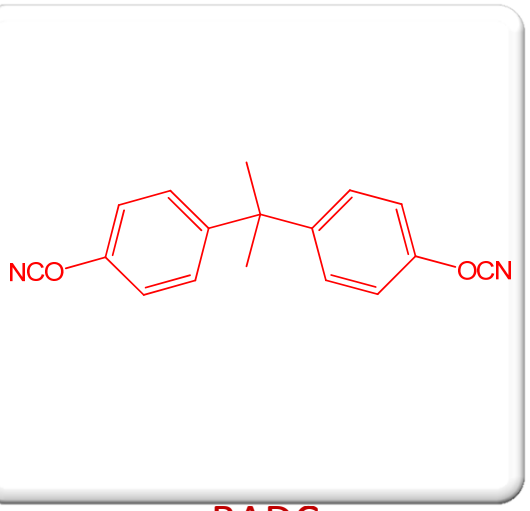


Error characteristics of partial least squares model for glass transition temperature at full cure.

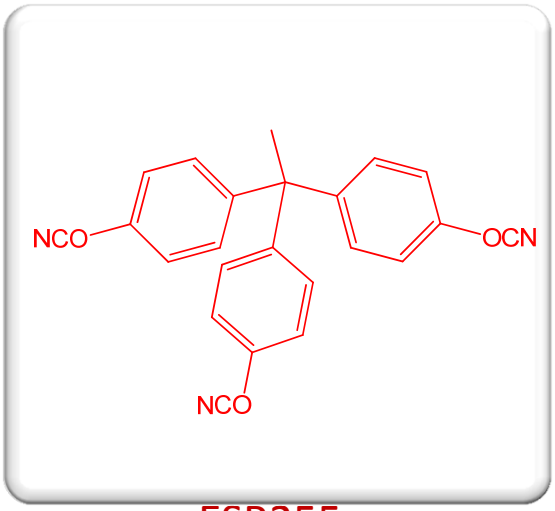
These results indicate there are only about 4 important structural parameters

Effects of topology are not considered

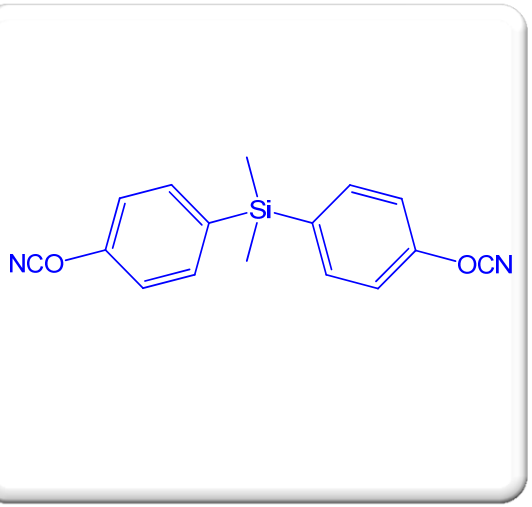
Example: Bias in Predictive Parameter Sets



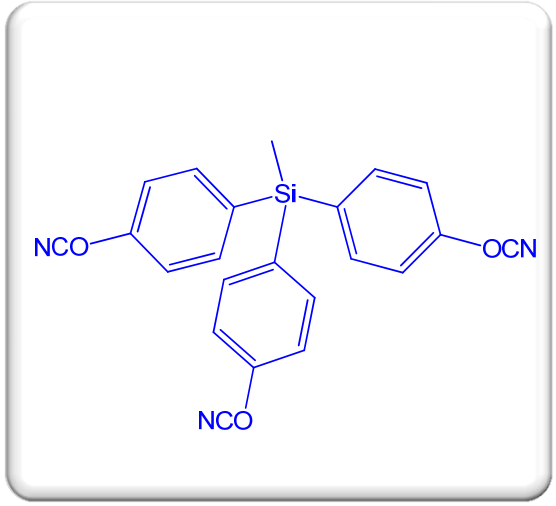
BADCy



ESR255



SiMCy



STT3

All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N_2, cure schedule for 1 hr at 150 °C followed by 24 hrs at 210 °C, with ramp rates at 5 °C / min.

In this case, we are interested in comparing models for two different architectures, one very common, the other somewhat rare

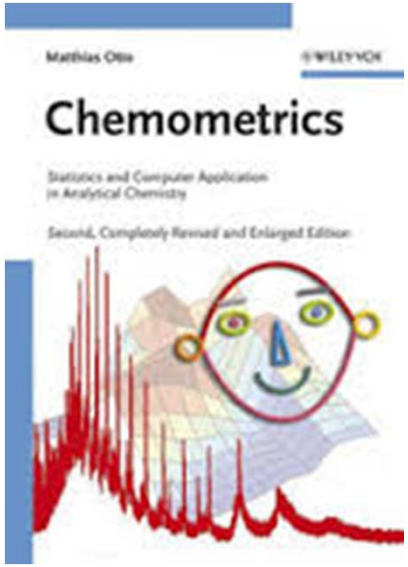
Comparison of Predicted and Experimental Melting Properties

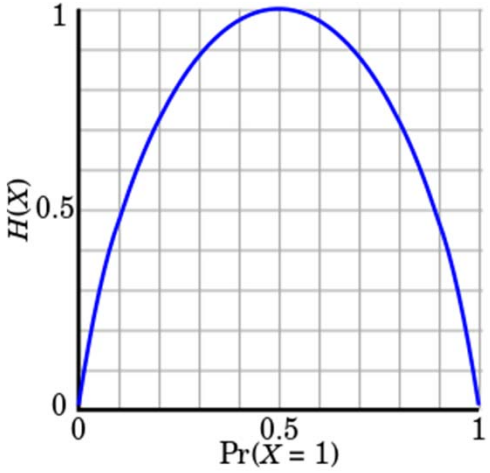
ΔS_m (kJ/mol K, monomer)	BADCy	SiMCy	ESR255	STT3
ΔS_m (kJ/mol K, Yalkowsky)	84	84	98	98
ΔS_m (kJ/mol K, experiment)	80.0 ± 1.4	82.1 ± 0.6	75.0 ± 1.9	74.8 ± 0.8
ΔS_m^0 (kJ/mol K, Chickos)	70	78	88	95
ΔS_m^0 (kJ/mol K, experiment)	69 ± 3	81 ± 1	50 ± 14	55 ± 3
T_m (model ΔS_m & exp. ΔH_m)				
Yalkowsky (°C)	66	54	24	24
Chickos (°C)	73	50	42	29
Experiment (°C)	82.1 ± 0.2	60.4 ± 0.1	115.9 ± 0.2	117.5 ± 0.1

- **Yalkowsky model over-predicts entropy of melting for tricyanates, in part because the rules for counting anisotropy do not consider star-like arrangements, and a triphenyl substituted *sp³* is still counted as flexible. These factors explain about 70% of the error.**
- **Chickos model has a similar pattern of predictive success, perhaps because "bis-like" prolate organic compounds are more studied than "tris-like" "pitchfork" structures**

Conversion from ΔS_m^0 to ΔS_m based on $\Delta_{cp,m}$ = const. = ΔS_m; $\Delta S_m = \Delta S_m^0 / [1 - \ln (T_m / 298)]$

Predictive Parameter Sets, M&S, Databases, and Heuristics





Author: Broma and Alessio Damato

- **A new bit of data for a database is most valuable when it describes the least known aspect of the data**
- **Good M&S can derive rules (such as elastic modulus as a function of topology) for reliably estimating the lesser known parameters from accessible experiments**
- **Databases and heuristics can be used to train and validate predictive systems, but are poor substitutes for QSARs**

Summary

- Significant advances in materials science for composites can be achieved by moving from a “heuristic classification” approach to an “informatics” approach to describe chemistry
- Although end-group chemistries play an important role as a predictive factor in composite resin processing and performance, they exist within a framework of structure-architecture-topology; often, other parts of the framework are more important predictors of performance
- Even complex polymer network structures can be described in terms of a comparatively small number of predictive parameter sets; fundamental scientific insight and access to a variety of chemical structures is required in order to understand what the most valuable predictive parameters are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